

CONTROLLABLE AND RAPID SOLUBILITY RATE OF WATER-SOLUBLE POLYMERIC FILMS

Field of the Invention

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[0001] This invention relates to compositions of polymer blends useful for preparing films by conventional industrial film processes, and particularly to water-soluble and heat-sealable films having a controlled water-solubility rate.

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Background of the Invention

[0002] Considerable interest has been shown recently in the use of polyvinyl alcohol water-soluble films for packaging and bags. Such products have a number of uses. Packaging materials contaminated by toxic or harmful materials such as biocides, preservatives, bleach, fertilizers and detergents, must be disposed in an environmentally safe way. Under increasing pressure of environmental regulation, it is often difficult and expensive to dispose of empty packages or bags which contain residues of toxic or harmful materials. It is highly desirable for the safety of the user of such toxic or harmful materials to use water-soluble polymer films as packaging films. Most of these chemicals are in powder or dust form and a user may breathe or be exposed to them. To protect a user from these chemicals, water-soluble bags can be used. When the chemical product is needed, the package is immersed in water and the package dissolves in water with its content. Airborne contamination is therefore eliminated.

[0003] For convenience of use and to reduce handling, many chemical products are packaged in unit containers or bags having a pre-determined quantity. For example, products such as dyes, detergents and cement are packaged in unit containers or bags. The use of such containers or bags permits measured amounts of the packaged chemicals

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to be used without handling the chemicals directly, protecting users from being exposed to the chemicals. Water-soluble films are suitable materials to prepare such unit containers or bags. When the chemical product is needed, the container or bag is immersed in water and the
5 bag and its content dissolves in water.

[0004] In the healthcare field, articles such as bedclothes from hospitals, particularly from infectious disease hospitals, have to be sterilized for reuse. It is important to protect workers from contact and
10 exposure to the used articles. Bags prepared from water-soluble films can be used as a container and put into a sterilizer directly without opening, to eliminate contact with infectious disease bacteria.

[0005] Water-soluble bags prepared from polymeric films are
15 particularly useful where the contents are toxic or should for other reasons not be touched.

[0006] Water-soluble films are also widely used in immersion printing processes. These are processes for decorating products with
20 complex curving surfaces. Water-soluble films can suitably be used as carriers of immersion printing plates. In immersion printing processes, controlled water-solubility rate and stiffness are both very important to the films floated on the water surface.

25 [0007] Many techniques have been investigated to modify polyvinyl alcohol to increase the water-solubility rate of films prepared therefrom. They can be summarized as following: (1) degradation of the polymer; (2) design of film structure; (3) new copolymers of polyvinyl alcohol; and (4) modifications of polyvinyl alcohol.

- 5 **[0008]** U.S. Patent No. 6,071,618 (Cook, Jr. et al.) discloses a process for increasing the solubility rate of a water soluble polyvinyl alcohol film. A polymeric film comprises at least one irradiated water soluble layer. In the irradiation process, the film is subjected to an energetic radiation treatment, such as corona discharge, plasma, flame, ultraviolet, X-ray, gamma ray, beta ray, and high energy electron treatment. The molecular weight of the polymer is decreased by the degradation of the polymer through the irradiation process to increase the solubility rate of the polymer. The molecular weight of the polymer is increased by crosslinking of the polymer through the irradiation process to decrease the solubility rate of the polymer. The irradiation equipment and process are very expensive. The patent indicates that the water-solubility rate of the films at 0°C can be increased.
- 15 **[0009]** U.S. Patent No. 3,387,405 (Iwasyk et al.) discloses a foam structure film of polyvinyl alcohol. A polyvinyl alcohol solution containing gelling agents is mixed with bubbles of air under pressure. The foam is dried to a cellular film to improve the water solubility rate. It is a slow process and difficult to control the gelling conditions.
- 20 **[0010]** U.S. Patent No. 3,157,611 (Lindemann) discloses a polyvinyl alcohol film plasticized by phosphate ester to improve the cold water solubility rate. It also indicates that many plasticizers such as glycerin, ethylene glycol, ethanol acetamide and ethanol formamide have been suggested for polyvinyl alcohol in order to produce a material readily dissolved in water but that they are not effective in producing polymeric materials with improved cold water solubility. The plasticizers disclosed in this patent have the following disadvantages: they are humectants which absorb moisture in high humidity conditions to make them become tacky and weak; or they are volatile so that they are easy to migrate to their surface. All these disadvantages will affect
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the water solubility rate and other physical properties of the film. The fact that phosphate esters are not highly compatible with polyvinyl alcohol results in the former tending to migrate to the surface of the latter.

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[0011] U.S. Patent No. 2,948,697 (Robertson) discloses that polyvinyl alcohol films plasticized by combination of polypropylene glycol and phosphate esters are improved in their water solubility rates both at high and low temperatures. But they still suffer two problems, namely poor compatibility between polyvinyl alcohol and plasticizers, and the migration of plasticizers to the surface of the films.

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[0012] U.S. Patent No. 3,106,543 (Milne) discloses a polyvinyl alcohol modification method: an ethylene oxide is reacted with aqueous polyvinyl alcohol solution to obtain a hydroxyethylated polyvinyl alcohol. The films prepared from the modified polyvinyl alcohol do not contain any plasticizers. Because the process must be carried out in extremely dilute aqueous polyvinyl alcohol solution in an autoclave, it is expensive.

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[0013] U.S. Patent No. 3,505,303 (Lindemann) discloses a film made of modified polyvinyl alcohols, which is clear, colorless and readily soluble in cold water. The patent indicates that the solubility of a film can be raised by modifying polyvinyl alcohol through copolymerization, but the solubility of a film in cold water is not increased. The films disclosed have high solubility in cold water. Under alkaline condition, acryl amide is added to some of the hydroxyl groups of the polyvinyl alcohol molecules by an alkene addition reaction. Because the concentration of the polyvinyl alcohol solution is 10-20%, the process is expensive. In addition, the acryl amides must be recovered.

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[0014] It would be desirable to provide water-soluble films having the characteristics of controllable solubility rate and rapid cold water solubility, even at 0°C.

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Summary of the Invention

[0015] According to one broad aspect of the invention, there is provided a water-soluble film comprising a blend of polyvinyl alcohol and a polymer containing a sulfonate monomer. According to another broad aspect of the invention, there is provided a composition comprising such blend for use in forming water-soluble films.

[0016] The invention provides controllable and rapid solubility rate of water-soluble polymeric films. The solubility rate of the polymeric films of the novel polymer blends is controlled by varying the weight percent of the sulfo-containing polymer in the composition of the polymer blend. The higher the weight percent of the sulfo-containing polymer in the composition of the polymer blend, the more rapid the solubility of the polymeric film. The solubility rate is increased at high or low temperatures, even at 0°C.

[0017] When the polymeric films of the present invention are immersed in water or floated on the surface of water, their water solubility can be controlled at a desired rate. The polymeric films can be used for packaging films and as a base materials of an immersion transfer printing film.

Detailed Description of the Preferred Embodiments

[0018] The present invention provides polymer blend compositions of polyvinyl alcohol and sulfonate polymers. The polymeric films prepared from novel compositions of the invention can be obtained by conventional industrial processes for film forming.

[0019] In this specification, the term "sulfo group" means the functional group of sulfonic acid in the form of free acid or its salts, i.e. $-\text{SO}_3\text{M}$, where M is H or a cation. The term "sulfonate monomer" means a monomer containing a sulfo group. The term "sulfonate polymer" means a polymer containing a sulfonate monomer. Thus, the sulfonate polymers of the invention are polymers containing a sulfo group.

[0020] It is important that the sulfonate polymers be water soluble. Accordingly, polymers with sulfo groups in the form of salts which render the polymers water insoluble, or minimally soluble, are not suitable for use in the invention. Preferably, the sulfonate polymers have sulfo groups in the form of the free acid or the sodium, potassium or ammonium salt, all of which are water soluble. The lithium salt is also useful, but is not preferred due to the higher cost of lithium salts. "Water soluble" in this specification means that the sulfonate polymer is readily soluble in water to an extent such that films comprising the polymer blend compositions of the invention are commercially-practical water-soluble films.

[0021] As used in this application, the term "polymers" is used generically, unless otherwise indicated, to mean homopolymers, copolymers, terpolymers, tetrapolymers, etc., and thus includes polymers prepared using any number of monomers. The term

- “copolymer” is used generically, unless otherwise indicated, to mean polymers prepared using more than one different monomers. The term “terpolymer” is used generically, unless otherwise indicated, to mean polymers prepared using three different monomers. The term
- 5 “tetrapolymer” is used generically, unless otherwise indicated, to mean polymers prepared using four different monomers.

- [0022] The sulfonate polymers can include polymers formed by the free-radical homo-polymerization or free-radical copolymerization of
- 10 sulfonate monomers. Non-limiting examples of suitable sulfonate monomers include ones from the following compounds: 2-chloroethylene sulfonic acid, ethylenesulfonic acid, ethylenedisulfonic acid, 1-nitriloethylenesulfonic acid, 2-formylethylenesulfonic acid; 1-carboxyethylenesulfonic acid; 1-propene-1-sulfonic acid; 1-propene-2-
- 15 sulfonic acid; 2-formyl-1-methylethylene sulfonic acid; 1-carboxy-2-methylethylene sulfonic acid; 2-methyl-1,3-propenedisulfonic acid; 1-butene-1-sulfonic acid; 1-carboxy-2,2-dimethyl-ethylene sulfonic acid; 1-pentene-1-sulfonic acid; 1-hexene-1-sulfonic acid; 2-(p-nitrophenyl) ethylene sulfonic acid; 2-phenylethylene sulfonic acid; 2-(p-
- 20 hydroxyphenyl) ethylene sulfonic acid; 2-(2-aminophenyl) ethylene sulfonic acid; 1-methyl-2-phenylethylene sulfonic acid; 2-(p-methoxyphenyl) ethylene sulfonic acid; 4-phenyl-1,3-butadiene sulfonic acid; 2-(p-acetamidophenyl) ethylene sulfonic acid; 3-chloroallyl sulfonic acid; allyl sulfonic acid; 1-hydroxyallyl sulfonic acid; 2-
- 25 cynoallyl sulfonic acid; 3-chloromethallyl sulfonic acid; 1-carboxyallyl sulfonic acid; 3-carboxyallyl sulfonic acid; methallyl sulfonic acid; 2-methylene-4,4-dimethyl-1,3-disulfo-pentene; 4-methylene-4,4-dimethyl pentene sulfonic acid; 1-hydroxy-3-phenylallyl sulfonic acid; 3-phenylallyl sulfonic acid; 2-benzylallyl sulfonic acid; 2-(p-
- 30 methylphenoxy) allyl-sulfonic acid; 3-phenoxy-methallyl sulfonic acid; 2-sulfoethyl acrylate; 2-sulfoethyl maleate; 3-sulfopropyl acrylate; 2-

sulfonyl methacrylate; 3-sulfopropyl acrylate; 2-sulfo-1-(sulfomethyl) ethyl methacrylate; 3-sulfopropyl maleate; 4-sulfobutyl methacrylate; 2-(acyloxymethyl)-c-sulfuran; bis-2-sulfoethyl fumarate; 3-sulfopropyl itaconate; p-sulfophenyl acrylate; 2-(2-methylacryloxymethyl)-
5 sulfofuran; bis(2-sulfoethyl) itaconate; p-sulfophenyl methacrylate; bis(3-sulfopropyl) maleate; bis(3-sulfopropyl) fumarate; bis (2-sulfopropyl) maleate; bis(2-sulfopropyl) fumarate; 5-methyl-2-(methallyloxy) benzene sulfonic acid; bis(2-sulfopropyl) itaconate; ar-(2-acryloyloxyethoxy)-2-naphthalene sulfonic acid; ar-(2-methacryloyloxyethoxy)-naphthalene sulfonic acid; dodecyl-4-
10 sulfopropyl itaconate; dodecyl-4-sulfobutyl itaconate; n-acryloyl taurine; allylthioethyl sulfonic acid; alloxy propene sulfonic acid; n-allyl-n-methylaminoethane-sulfonic acid; n-(methacrylamidomethyl)-sulfoacetamide; vinyloxybenzene sulfonic acid; n-(p-sulfophenyl)
15 methacrylamide; p-[(2-vinylsulfonyl)ethoxy]-benzene sulfonic acid; n-methyl-n-(2-vinylsulfonyl-ethyl)-p-(sodiumsulfo) benzyl amine; dichlorostyrene sulfonic acid; 2-chlorostyrene sulfonic acid; p-styrene sulfonic acid; p-sulfonic acid; vinyltoluene sulfonic acid; 2-methyl styrene sulfonic acid; the potassium, sodium and ammonium salts of
20 each of the foregoing compounds; 4-methylene-2,2,6,6-tetramethyl-3,5-disulfoheptene; allyloxyethyl sulfonic acid; allyl oxybenzene sulfonic acid; and styrene sulfonic acid.

[0023] The sulfonate polymers of the invention can be obtained by
25 the free-radical copolymerization of a sulfonate monomers and an olefinic co-monomer. Non-limiting examples of suitable olefinic co-monomers include ones from the following compounds and groups: acrylic acid and its salt; methacrylic acid and its salt; acrylates; methacrylates; acrylamide; methacrylamide; vinyl acetate; n-vinyl
30 pyrrolidon; styrene; vinyl chloride; acrylonitrile; and allyl.

[0024] Free radical initiators that may be used include 2,2'-azobisisobutyronitrile, acetyl peroxide, benzoyl peroxide, t-butyl peroxide, cumyl peroxide, t-butylhydro peroxide, cumylhydro peroxide, hydrogenperoxide-ferrous sulfate.

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[0025] The sulfonate polymers can be prepared by any conventional free radical polymerization technique, such as solution polymerization, suspension polymerization, emulsion polymerization and bulk polymerization.

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[0026] The sulfonate polymers may also be formed by the condensation polymerization of formaldehyde with sulfonate monomers, including sulfonate monomers of the following compounds:
aminotoluene sulfonic acid; aminophenol sulfonic acid; 2-amino-4-chloro-phenyl sulfonic acid; 2-amino-1-naphthalene sulfonic acid; 1-amino-8-naphthol-3,5 disulfonic acid; amino-naphthalene trisulfonic acid; aminobenzene-2,5 disulfonic acid; diaminostilbene sulfonic acid; phenol sulfonic acid; amino-naphthol disulfonic acid; and aminodiphenylamine methane sulfonic acid.

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[0027] The sulfonate polymers may also be formed by direct sulfonation or alkyl-sulfonation of the polymers. Sulfonation and alkyl-sulfonation reagents include sulfur trioxide and its complex, sulfuric or chlorosulfonic acid, sultone and acetyl sulfate.

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[0028] The sulfonate polymers can include sulfonated polystyrene, sulfonated polysulfone, sulfonated melamine-formaldehyde resin, sulfonated phenol-formaldehyde resin, sulfonated urea-formaldehyde resin, sulfonated naphthalene-formaldehyde resin, sulfonated ethyl cellulose, sulfonated polyurethane, sulfonated polypropylene glycol, and sulfonated polyethylene glycol.

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[0029] The number average molecular weight of the sulfonate polymers of the invention is in the range of about 18,000 - 26,000, preferably 19,000 - 23,000. The number average molecular weight of the polyvinyl alcohol used for present invention is in the range of about 7,000 - 13,000, preferably 8,000 - 11,000.

[0030] The polymer blends of the present invention preferably contain sulfonate polymers in the range of about 0.01 - 60% by weight of the blend, more preferably 0.1 - 50% by weight, more preferably 1 - 45% by weight, and most preferably 1 - 40% by weight. Said blends can be prepared by any conventional industrial process for preparing polymer blends, of which a mixing process is preferred.

[0031] The polymeric films prepared from the blends may include conventional film forming additives, including wetting agents, fillers, plasticizers, antioxidants, mold releasing agents, biocides, anti-blocking agents, defoamers, lubricants, etc. Depending on the compositions of the blends, the quantity of the additives is typically 0.1 - 18 weight %.

[0032] The polymeric films can be prepared by any conventional film process, of which solution casting, melt extrusion and blown film processes are more preferred.

[0033] The water solubility rate of the polymeric films can be controlled by varying the compositions of the polymer blend. The water solubility rate of the films depends directly on the weight percent of the sulfonate polymers in the blends. The weight percent of the sulfonate polymers in the blends controls the water solubility rate of the films.

The water solubility rate of the polymeric films prepared from the novel

polymer blends can be increased to 2.4 times of that of a polyvinyl alcohol film at the temperature of 0°C.

[0034] In the following examples, the polyvinyl alcohol used has a
5 number average molecular weight of 7,000 - 13,000; and the poly
sodium styrene sulfonate used has a number average molecular weight
of 18,000 to 26,000.

Example 1

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A polymer blend of 90% by weight of polyvinyl alcohol and 10% by
weight of poly sodium styrene sulfonate was prepared. The two
components were premixed and then pelletized. The composition was
formed into a film by means of a blown film process at 200 °C.

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Example 2

A polymer blend of 80% by weight of polyvinyl alcohol and 20% by
weight of poly sodium styrene sulfonate was prepared. The two
20 components were premixed and then pelletized. The composition was
formed into a film by means of a blown film process at 200 °C.

Example 3

25 A polymer blend of 70% by weight of polyvinyl alcohol and 30% by
weight of poly sodium styrene sulfonate was prepared. The two
components were premixed and then pelletized. The composition was
formed into a film by a blown film process at 200 °C.

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Example 4

For comparative purposes a film was made without a sulfonate polymer. A film was cast from an aqueous polyvinyl alcohol solution, the
5 concentration and the average MW of which are 18 wt% and 7,000 - 13,000, respectively. The solution was poured onto a glass plate and is spread into a uniform film by a glass bar. It was dried for 24 hours at a temperature of 45°C. The dried film was peeled off from the glass
10 plate.

The water solubility rates of the films produced in Examples 1 to 4 were measured. Films of 4 cm x 1 cm x 0.03 cm (thickness) were used. 250 ml of water in a 500 ml beaker was held at 15°C and constantly stirred. The films were put in the water and permitted to dissolve. The water
15 solubility rate was measured as the time interval between the moment the film touched the water and the moment the film disappeared by visual inspection. The results are summarized in Table 1.

Table 1: Controllable Water Solubility Rate of the Films

	Compositions of the Films (wt%)		Water Solubility Rate at 15°C (Sec.)
	A	B	
Ex. 1 Film	90	10	10.2
Ex. 2 Film	80	20	8
Ex. 3 Film	70	30	3
Ex. 4 Film	100	0	14.2

A = Polyvinyl alcohol
B = Poly sodium styrene sulfonate

30 The water solubility rates of the Example 1 film, Example 2 film and Example 3 film are 1.4, 1.8 and 8 times faster than that of Example 4 film, respectively.

Example 5

A blend of 91% by weight of polyvinyl alcohol and 9% by weight of poly sodium styrene sulfonate was prepared, with 12.6% by weight
5 (based on the total weight of the polymers) of propylene glycol, 1.7% by weight of sodium C₁₂₋₁₆ olefin sulfonate and 1.7% dihydroxy ethylphenol amine. The components were premixed and then pelletized. The composition was formed into a film by a blown film process at 195°C.

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Example 6

For purposes of comparison with the film of Example 5, a film was made without the poly sodium styrene sulfonate. A blend of 100% by weight of polyvinyl alcohol was prepared with 12.6% by weight (based
15 on the total weight of the polyvinyl alcohol) of propylene glycol, 1.7% by weight of sodium C₁₂₋₁₆ olefin sulfonate and 1.7% by weight of dihydroxy ethylphenol amine. The components were premixed and then pelletized. A film was formed into a film by a blown film process at 198°C.

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The water solubility rates of the films produced in Examples 5 and 6 were measured (at 25°C) by the method described above in Example 4. The results are summarized in Table 2.

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Table 2: Water Solubility Rate at 25°C.

Film Compositions (wt%)				Water Solubility Rate at 25°C (Sec.)
	A	B	C	
Example 5	91	9	16	4
Example 6	100	0	16	8.4

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A = Polyvinyl alcohol
B = Poly sodium styrene sulfonate

C = Propylene glycol 12.6wt%; sodium C₁₂₋₁₆ olefin sulfonate 1.7wt%; and dihydroxy ethylphenol amine 1.7wt%. Weight percentages are relative to the total weight of the polymers only.

- 5 The water solubility rates of the Example 5 film is 2.1 times faster than that of Example 6 film, at 25°C.

The water solubility rates of these films was then measured at 0°C, using the same method. The results are summarized in Table 3.

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Table 3: Water Solubility Rate at 0°C.

Film Compositions [wt%]				Water Solubility Rate at 0°C [Sec.]
	A	B	C	
Example 5	91	9	16	9.4
Example 6	100	-	16	22.4

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A = Polyvinyl alcohol
B = Poly sodium styrene sulfonate
C = Propylene glycol 12.6wt%; sodium C₁₂₋₁₆ olefin sulfonate 1.7 wt%; and dihydroxy ethylphenol amine 1.7wt%. Weight percentages are relative to the total weight of the polymers only.

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The water solubility rates of the Example 5 film is 2.4 times faster than that of the Example 6 film, at 0°C.

- 25 **[0035]** As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the spirit or scope thereof. Accordingly, the scope of the invention is to be construed in accordance with the substance defined by the following
- 30 claims.